

A SILOXANE-BASED RESIN CONTAINING GERMANIUM AND AN
INTERLAYER INSULATING FILM FOR A SEMICONDUCTOR DEVICE USING
THE SAME

BACKGROUND OF THE INVENTION

[0001] This non-provisional application claims priority under 35 U.S.C. § 119(a) on Korean Patent Application No. 2003-47731 filed on July 14, 2003, which is herein incorporated by reference.

FIELD OF THE INVENTION

[0002] The present invention relates to a siloxane-based resin and an interlayer insulating film for a semiconductor device formed using the same. More specifically, the present invention relates to a siloxane-based resin containing germanium and a resinous film useful as an insulating film between interconnecting layers of a semiconductor device.

DESCRIPTION OF THE RELATED ART

[0003] As the circuit density of multilevel integrated circuit devices increases,

the size feature of a semiconductor device is constantly required to be reduced. The chief obstacle to the feature of size reduction of a semiconductor device is the $R(\text{resistance}) \times C(\text{capacitance})$ delay due to crosstalk between interconnecting layers. A solution to this problem is to lower the dielectric constant of interlayer insulating films so as to decrease the $R \times C$ delay as much as possible. So, there have been various attempts to provide an insulating film having a low dielectric constant.

[0004] Conventionally, in the field of semiconductor devices, interlayer insulating films have been formed by a CVD (chemical vapor deposition) method using SiO_2 having a dielectric constant of 4.0. However, US Patent Nos. 3,615,272; 4,399,266; 4,756,977 and 4,999,397 disclose the formation of insulating films by the SOD (spin on deposition) method using polysilsesquioxanes having dielectric constants of 2.5-3.1 as well as good planarization properties.

[0005] Hydrogen silsesquioxanes as well as preparation methods thereof are well known in the art. For example, US Patent No. 3,615,272 discloses a method of preparing a completely condensed, soluble hydrogen silsesquioxane resin, which comprises the steps of condensing trichlorosilanes in a sulfuric

acid medium and washing the resulting resin with water or aqueous sulfuric acid. Also, US Patent No. 5,010,159 discloses a method of synthesizing a soluble condensed hydrogen silsesquioxane resin, which comprises the steps of hydrolyzing hydrosilanes in an arysulfuric acid hydrate-containing hydrolysis medium and contacting the resulting resin with a neutralizing agent. US Patent No. 6,232,424 describes a highly soluble silicon resin composition having excellent solution stability, which is prepared by hydrolyzing and polycondensing tetraalkoxysilane, organosilane and organotrialkoxysilane monomers in the presence of water and a catalyst. US Patent No. 6,000,339 describes that a silica-based compound is useful for improving the resistance to oxygen plasma and physical properties as well as the thickness of a coating film, which can be obtained through reacting a monomer selected from the group consisting of alkoxysilane, fluorine-containing alkoxysilane and alkylalkoxysilane with a titanium- or zirconium-alkoxide compound in the presence of water and a catalyst. US Patent No. 5,853,808 discloses that siloxane and silsesquioxane polymers useful for forming a SiO₂-rich ceramic coating can be obtained from hydrolysis and polycondensation of organosilanes having a β -substituted alkyl group. Meanwhile, EP 0 997 497

A1 discloses that hydrolyzation and polycondensation of a certain combination of alkoxysilanes including mono-, di-, tri-, tetraalkoxysilane and trialkoxysilane dimers can provide resinous materials for insulating films.

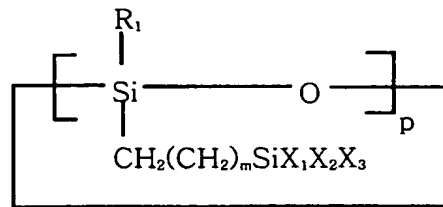
SUMMARY OF THE INVENTION

[0006] The present invention features the production of a siloxane-based resin having excellent mechanical properties as well as a very low dielectric constant, and the formation of a low dielectric insulating film using the siloxane-based resin.

[0007] That is, the present provides a siloxane-based resin having superior mechanical properties, wherein a germanium-containing monomer, subjected to sol-gel polymerization, is provided to increase the mechanical properties with no reduction of the dielectric constant of the siloxane-based resin. The germanium monomer has twice the density compared with the siloxane-based monomer, and thus can provide an improvement in the mechanical properties.

[0008] One aspect of the present invention relates to a siloxane-based resin that is prepared by hydrolyzing and polycondensing a first monomer of the Formula 1 and a second monomer of Formula 2 in an organic solvent in the presence of an acid or alkaline catalyst and water:

Formula 1



wherein,

R_1 is a hydrogen atom, a C_{1-3} alkyl group, or a C_{6-15} aryl group;

X_1 , X_2 and X_3 are independently a C_{1-3} alkyl group, a C_{1-10} alkoxy group, or a halogen atom, provided that at least one of X_1 , X_2 and X_3 is hydrolysable;

p is an integer of 3-8; and

m is an integer of 0-10, and

Formula 2



wherein,

R_2 is a hydrogen atom, a C_{1-3} alkyl group, or a $\text{C}_6\text{-C}_{15}$ aryl group;

X_4 is a C_{1-10} alkoxy group, or a halogen atom; and

a is an integer of 1-4.

[0009] Another aspect of the present invention relates to a method of forming an insulating film between interconnecting layers of a semiconductor device,

the method comprising the steps of: providing a resin solution by dissolving the inventive siloxane-based resin in an organic solvent; coating a silicon wafer with the resin solution; and heat-curing the resulting coating film.

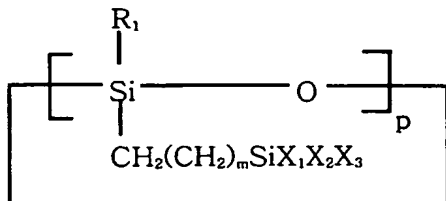
[0010] Still another aspect of the present invention relates to an interlayer insulating film made using the inventive siloxane-based resin.

[0011] All of the above features and other features of the present invention will be successfully achieved by following the teachings of the present invention described in the following.

DESCRIPTION OF THE PREFERRED INVENTION

[0012] The present invention provides a siloxane-based resin having a dielectric constant of 3.0 or less through the polycondensation of a cyclic siloxane monomer of the Formula 1 and a compound containing germanium of the Formula 2:

Formula 1



wherein,

R_1 is a hydrogen atom, a C_{1-3} alkyl group, or a C_{6-15} aryl group;

each of X_1 , X_2 and X_3 , independently, are a C_1-C_3 alkyl group, a C_1-C_{10} alkoxy group, or a halogen atom; provided that at least one of them is hydrolysable;

p is an integer of 3-8; and

m is an integer of 0-10; and

Formula 2



wherein,

R_2 is a hydrogen atom, a C_{1-3} alkyl group, or a C_{6-15} aryl group;

X_4 is a C_{1-10} alkoxy group, a halogen atom; and

a is an integer of 1-4.

[0013] In the preparation of the inventive siloxane-based resin, the monomer of the Formula 1 and the monomer of the Formula 2 are mixed in a molar ratio of 1:99 -99:1.

[0014] Preferable acid or base catalyst for the preparation of the inventive siloxane-based resin can be exemplified by, but are not limited to, hydrochloric

acid, nitric acid, benzene sulfonic acid, oxalic acid, formic acid, potassium hydroxide, sodium hydroxide, triethylamine, sodium bicarbonate and pyridine.

Such a catalyst is used so that molar ratio of the catalyst to the monomers is 0.00001:1 - 10:1.

[0015] The amount of water used in the preparation of the inventive siloxane-based resin is 1-1000mol per 1mol of the monomers, so that molar ratio of water to the monomers is 1:1-100:1.

[0016] Non-limiting examples of the organic solvent used in the preparation of the inventive siloxane-based resin include aliphatic hydrocarbon solvents such as hexane; aromatic hydrocarbon solvents such as anisole, mesitylene and xylene; ketone-based solvents such as methyl isobutyl ketone, 1-methyl-2-pyrrolidinone and acetone; ether-based solvents such as cyclohexanone, tetrahydrofuran and isopropyl ether; acetate-based solvents such as ethyl acetate, butyl acetate and propylene glycol methyl ether acetate; alcohol-based solvents such as isopropyl alcohol and butyl alcohol; amide-based solvents such as dimethylacetamide and dimethylformamide; silicon-based solvents; and mixtures thereof.

[0017] According to the present invention, the hydrolysis and

polycondensation reaction is carried out at a temperature of 0-200°C, for 0.1-100hrs, preferably 5-48hrs.

[0018] The siloxane-based resin thus prepared has Mw of 3,000-300,000.

[0019] The present invention also provides a method of forming an interlayer insulating film for a semiconductor device using the inventive siloxane-based resin. The insulating film has a low dielectric constant, 3.0 or less and exhibits excellent mechanical and heat resistance properties. According to the present invention, such an insulating film can be obtained by coating a silicon wafer with a solution containing the inventive siloxane-based resin in an organic solvent and heat-curing the resulting coating film. That is, the inventive siloxane-based resin dissolved in an organic solvent is applied onto a substrate. Then, the organic solvent is evaporated through simple air-drying or by subjecting the substrate, at the beginning of following heat-curing step, to vacuum conditions or to mild heating at a temperature of 200°C or less, so that a resinous coating film can be deposited on the surface of the substrate. Thereafter, the resinous coating film is cured by heating the substrate at a temperature of 150-600°C, preferably 200-450°C, for 1-150 minutes to provide an insoluble, substantially crack-free film. As used herein, by "crack-free

film” is meant a film without any crack that can be observed with an optical microscope at a magnification of 1000X. As used herein, by “insoluble film” is meant a film that is substantially insoluble in any solvent described as being useful for dissolving the inventive siloxane-based resin.

[0020] According to the present invention, the combined use of a porogen with the inventive siloxane-based resin may further lower the dielectric constant of the final insulating film down to 2.50 or less. As used herein, by “porogen” is meant any pore-generating compounds. In case of using porogen, an additional step is required of heating the resinous film over the decomposition temperature of the porogen so that the porogen can be decomposed.

[0021] The porogen used in the present invention may be any of the pore-generating compounds well known in the art, which can be exemplified by, but are not limited to, cyclodextrin, polycaprolactone, and derivatives thereof. The porogen is mixed with the inventive siloxane-based resin so that weight ratio of the porogen to the resin is 1:99-70:30, wherein both porogen and resin are in the form of solid powder.

[0022] Preferred organic solvents for the dissolution of the siloxane-based resin or the porogen to provide a liquid coating composition can be exemplified

by, but are not limited to, aliphatic hydrocarbon solvents such as hexane; aromatic hydrocarbon solvents such as anisole, mesitylene and xylene; ketone-based solvents such as methyl isobutyl ketone, 1-methyl-2-pyrrolidinone and acetone; ether-based solvents such as cyclohexanone, tetrahydrofuran and isopropyl ether; acetate-based solvents such as ethyl acetate, butyl acetate and propylene glycol methyl ether acetate; alcohol-based solvents such as isopropyl alcohol and butyl alcohol; amide-based solvents such as dimethylacetamide and dimethylformamide; silicon-based solvents; and mixtures thereof.

[0023] In the preparation of the liquid coating composition, the weight ratio of solid component containing the siloxane-based resin and the porogen is preferably 5-70 wt% based on the total composition. And the organic solvent should be used in an amount sufficient to apply the solid components including the siloxane-based resin and the porogen evenly to the surface of a wafer. Thus, the organic solvent should amount to 20-99.9wt%, preferably 70-95wt% of the liquid coating composition. If the organic solvent content of the liquid coating composition is less than 20wt%, part of the siloxane-based resin remains undissolved. On the other hand, if the organic solvent content is more than 99.9wt%, the final resinous film is as thin as 1000Å or less.

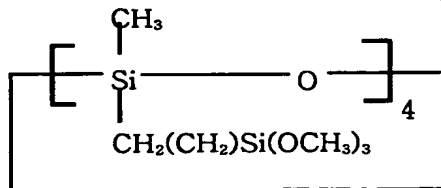
[0024] In the present invention, the liquid coating composition thus prepared can be applied to a silicon wafer according to various coating methods well known in the art. Non-limiting examples of the coating method useful in the present invention include spin-coating, dip-coating, spray-coating, flow-coating and screen-printing, while spin-coating is most preferred.

[0025] Hereinafter, the present invention will be described in more detail with reference to the following Examples. However, these Examples are given for the purpose of illustration and are not to be construed as limiting the scope of the present invention.

EXAMPLE 1: Synthesis of Monomer

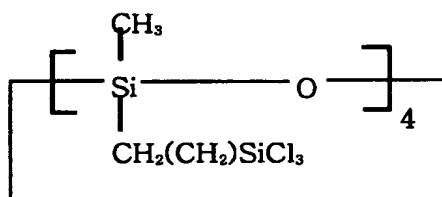
Example 1-1: Synthesis of Cyclic Siloxane-based Monomer (A)

Monomer (A)



[0026] To a flask are introduced 10.0g (29.014mmol) of 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane and 0.164g of platinum(O)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (solution in xylene), and then diluted

with 300ml of diethylether. Next, the flask is cooled to -78°C , 17.29g (127.66mmol) of trichlorosilane is slowly added thereto, and it is slowly warmed to room temperature. The reaction is continued at room temperature for 40hrs, and volatile materials are removed from the reaction mixture under a reduced pressure of about 0.1Torr. To the reaction mixture is added 100ml of hexane and stirred for 1hr, followed by filtering through celite to afford a colorless, clear solution. From the solution is then removed hexane under a reduced pressure to afford a liquid compound represented by the following Formula:



[0027] 10.0g (11.28mmol) of the liquid compound is diluted with 500ml of tetrahydrofuran, and 13.83g (136.71mmol) of triethylamine is added thereto. Thereafter, the mixture is cooled to -78°C , 4.38g (136.71mmol) of methyl alcohol is slowly added thereto, and it is slowly warmed to room temperature. The reaction is continued at room temperature for 15hrs and filtered through celite, and then volatile materials are evaporated from the resulting filtrate under a reduced pressure of about 0.1Torr. Subsequently, 100ml of pentane is added to the remaining filtrate and stirred for 1hr, followed by filtering

through celite. To the filtrate is added 5g of activated carbon and stirred for 10 hrs. Filtrate obtained from the filtration of the stirred solution is subjected to a reduced pressure to remove hexane therefrom and afford monomer (A) as a colorless liquid. The results obtained from NMR analysis of this monomer dissolved in CDCl_3 are as follows:

^1H NMR(300MHz) data ; δ 0.09 (s, 12H, 4 \times -CH₃),

0.52-0.64 (m, 16H, 4 \times -CH₂CH₂-),

3.58 (s, 36H, 4 \times -[OCH₃]₃)

Example 1-2: Synthesis of Germanium-based Monomer (B)

Monomer (B)



[0028] To a flask is introduced 19.3g (0.1mol) of trichloromethylgermanium, and then diluted with 500ml of tetrahydrofuran. Next, the flask is cooled to 0°C, 35.35g (0.35mol) of triethylamine is added thereto, followed by the slow addition of 11.2g (0.35mol) of methyl alcohol. Then the reaction temperature is slowly elevated to room temperature. The reaction is continued at room temperature for 15hrs. At the completion of the reaction, the reaction mixture is filtered through celite, and volatile materials are removed from the filtrate

under a reduced pressure of about 0.1 Torr. To the remaining filtrate is added 100ml of hexane and stirred for 1 hr, followed by filtering through celite. From the filtrate is then removed hexane under a reduced pressure to afford a colorless liquid. Colorless liquid monomer (B) is obtained from simple distillation of the liquid. The results obtained from NMR analysis of this monomer dissolved in CDCl_3 are as follows:

^1H NMR(300MHz) data ; δ 3.6 (s, 3H)

Example 1-3: Synthesis of Germanium-based Monomer (C)

Monomer (C)



[0029] Example 1-3 is carried out according to the same manner as in the above Example 1-2, except that methylalcohol is replaced with ethylalcohol.

[0030] The results obtained from NMR analysis of the monomer (C) thus prepared and dissolved in CDCl_3 are as follows:

^1H NMR(300MHz) data ; δ 1.2 (t, 6H, 3 \times -CH₃), δ 3.8 (q, 9H, 3 \times -CH₂)

Example 1-4: Synthesis of Germanium-based Monomer (D)

Monomer (D)



[0031] To a flask is introduced 21.4g(0.1mol) of tetrachlorogermanium, and then diluted with 500ml of tetrahydrofuran. Next, the flask is cooled to 0°C, 45.45g (0.45mol) of triethylamine is added thereto, followed by the slow addition of 14.4g(0.45mol)of methyl alcohol. Then the reaction temperature is slowly elevated to room temperature. The reaction is continued at room temperature for 15hrs. At the completion of the reaction, the reaction mixture is filtered through celite, and volatile materials are removed from the filtrate under a reduced pressure of about 0.1Torr. To the remaining filtrate is added 100ml of hexane and stirred for 1hr, followed by filtering through celite. From the filtrate is then removed hexane under a reduced pressure to afford a colorless liquid. Colorless liquid monomer (D) is obtained from simple distillation of the liquid. The results obtained from NMR analysis of this monomer dissolved in CDCl₃ are as follows:

¹H NMR(300MHz) data ; δ 1.2 (t, 8H, 4×-CH₃), δ 3.8 (q, 12H, 4×-CH₂)

EXAMPLE 2: Synthesis of Matrix Resin

[0032] The cyclic siloxane monomer (A) and one of the linear siloxane monomers (B) through (D) obtained from the above Example 1 are quantified respectively according to Table 1 below and introduced to a flask, followed by dilution with 15× tetrahydrofuran. Subsequently, after cooling the flask down to -78°C, certain amounts of deionized water and HCl are slowly added thereto. Then, the flask is warmed to 70°C, at which temperature the flask is left for 20hrs so that the reaction could continue. At the completion of the reaction, the reaction mixture is transferred to a separatory funnel, followed by addition of diethylether and tetrahydrofuran as much as the tetrahydrofuran used in the previous dilution of the monomer. Then, 3×washing is conducted, each round with water one tenth as much as the total solution in the separatory funnel. After washing, volatile materials are evaporated from the remaining solution to afford white powdery polymers. The powder is completely dissolved in a small amount of acetone to obtain a clear solution, and this solution is filtered through a 0.2µm syringe filter so as to remove impurities to provide a clear filtrate, to which is then slowly added deionized water. As a result, white powdery material is formed, which is then separated from the liquid

phase(mixed solution of acetone and water) and dried for 10 hrs at a temperature of 0-20°C under a reduced pressure of about 0.1Torr to afford a fractionated siloxane-based resin.

TABLE 1

Siloxane Resin	Monomer (mmol)				HCl(mmol)	H ₂ O(mmol)	Final Resin (g)
	(A)	(B)	(C)	(D)			
(a)	12.32	9.17			0.12	250	5.76
(b)	13.87	11.62			0.22	548	10.7
(c)	10.55	4.67			0.145	514	8.77
(d)	10.55		4.67		0.145	514	8.43
(e)	10.55			4.67	0.145	514	8.12
(f)	10.55			4.67	0.145	857	8.34
(g)	10.55			4.67	0.131	514	8.03
(h)	10.55			4.67	0.101	514	8.55
(i)	10.55			4.67	0.080	514	8.34
(j)	10.55			4.67	0.048	514	8.07

EXAMPLE 3: Measurement of Thickness and Refractive Index of Thin film

[0033] The siloxane-based resins obtained from the above Example 2, and their mixture with heptakis (2,3,6-tri-O-methoxy)- β -cyclodextrin are dissolved in propylene glycol methyl ether acetate (PGMEA), respectively, so that final concentration of the solid matter in the resulting liquid coating compositions is 25wt%. Each of the coating compositions is then spin-coated onto a silicon wafer for 30 seconds with maintaining the spin rate of 3,000rpm. In a nitrogen atmosphere, the coated wafers are subjected to the sequential soft baking on a hot plate (1min at 100°C and another minute at 250°C) so as to

evaporate the organic solvent sufficiently. Thereafter, the temperature is elevated to 420°C at a rate of 3°C/min under vacuum condition, at which temperature the coating films are allowed to cure for 1hr to afford test pieces.

[0034] Each of the test pieces thus prepared is analyzed for film thickness and refractive index. The film thickness and the refractive index are measured at 5 different points every test piece by the use of a profiler and a prism coupler, respectively. The mean thickness and refractive index are set forth in Table 3 along with their uniformity.

TABLE 2

Thin Film Composition			Thick. (Å)	Refractive Index	Uniformity of R.I (%)	Uniformity of Thick. (%)
Siloxane Resin	Resin (wt%)	Pore-forming Material (wt%)				
(a)	100	-	8995	1.3876	0.088	1.87
(a)	70	30	9846	1.3775	0.143	1.34
(b)	100	-	10254	1.3891	0.063	0.76
(b)	70	30	10457	1.4123	0.044	1.54
(c)	100	-	10334	1.4136	0.021	0.76
(c)	70	30	9765	1.3543	0.76	1.21
(d)	100	-	10923	1.4113	0.23	0.23
(d)	70	30	10654	1.3235	0.192	1.05
(e)	100	-	11129	1.3654	0.022	1.23
(e)	70	30	10537	1.3247	0.054	1.54
(f)	100	-	11587	1.3675	0.027	0.78
(f)	70	30	9976	1.3208	0.054	0.56
(g)	100	-	11034	1.3143	0.046	0.59
(g)	70	30	9861	1.3221	0.059	1.16
(h)	100	-	11738	1.3023	0.013	1.45
(h)	70	30	11587	1.3114	0.049	1.75
(i)	100	-	10987	1.4211	0.051	1.76
(i)	70	30	9398	1.4367	0.036	1.08
(j)	100	-	11456	1.4178	0.037	0.84
(j)	70	30	10324	1.3106	0.056	0.38

EXAMPLE 4: Measurement of Dielectric Constant of the Thin film

[0035] P-type silicon wafers doped with boron are coated with a 3000Å thermally-oxidized silicon film, followed by sequential deposition of a 100Å of titanium layer, a 2000Å of aluminum layer and a 100Å of titanium layer using a metal evaporator. On the surface of each of these wafers is formed a resinous film according to the same manner as in the above Example 3 in the composition of Table 3. Subsequently, on the resinous film is deposited a circular electrode of 1m diameter which consists of a 100Å-thick titanium layer and a 5000 Å-thick aluminum layer through a hard mask so as to provide a test piece having MIM (metal-insulator-metal) structure. Test pieces thus prepared are subjected to measurement of capacitance at 100kHz using PRECISION LCR METER (HP4284A) with Micromanipulator 6200 probe station. Dielectric constant of each test film is calculated from the following equation, wherein “d” value is obtained by the use of an ellipsometer:

$$k = C \times d / \epsilon_0 \times A$$

wherein,

k: dielectric constant

C: capacitance

ϵ_0 : dielectric constant in vacuum

d: the thickness of the low dielectric thin film

A: contact area of electrode

TABLE 3

Thin Film Composition			Dielectric Constant
Siloxane Resin	Resin (wt%)	Pore-forming Material (wt%)	
(a)	100	-	2.56
(a)	70	30	2.21
(b)	100	-	2.76
(b)	70	30	2.32
(c)	100	-	2.72
(c)	70	30	2.34
(d)	100	-	2.67
(d)	70	30	2.24
(e)	100	-	2.68
(e)	70	30	2.23
(f)	100	-	2.72
(f)	70	30	2.21
(g)	100	-	2.79
(g)	70	30	2.24
(h)	100	-	2.80
(h)	70	30	2.25
(i)	100	-	2.83
(i)	70	30	2.31
(j)	100	-	2.86
(j)	70	30	2.21

EXAMPLE 5: Measurement of Hardness and Modulus of the Thin film

[0036] Test pieces prepared as in the above Example 4 are analyzed for hardness and elastic modulus using Nanoindenter II (MTS Co.). The resinous film of each test piece is indented until the indentation depth reached 10% of its whole thickness. At this time, to secure the reliability of this measurement, 6 points are indented every test piece, and mean hardness and modulus are

taken. The results are set forth in Table 4.

TABLE 4

Thin Film Composition			Hardness (GPa)	Modulus (GPa)
Siloxane Resin	Resin (wt%)	Pore-forming Material (wt%)		
(a)	100	-	0.72	5.11
(a)	70	30	0.45	3.14
(b)	100	-	0.75	5.32
(b)	70	30	0.41	3.23
(c)	100	-	1.23	5.65
(c)	70	30	1.02	3.02
(d)	100	-	1.10	5.21
(d)	70	30	0.98	3.65
(e)	100	-	1.42	6.58
(e)	70	30	1.11	3.63
(f)	100	-	1.34	6.89
(f)	70	30	0.99	3.87
(g)	100	-	1.09	6.52
(g)	70	30	0.77	3.55
(h)	100	-	1.17	6.16
(h)	70	30	0.54	3.67
(i)	100	-	1.14	6.21
(i)	70	30	0.59	3.48
(j)	100	-	1.04	6.97
(j)	70	30	0.64	3.30

COMPARATIVE EXAMPLE 1: Synthesis of Siloxane-based Resin

[0037] The cyclic siloxane monomer (A) and one of the methyl trimethoxysilane monomer (B') or tetraethoxysilane monomer (D') are introduced to a flask, followed by dilution with 15× tetrahydrofuran. Subsequently, after cooling the flask down to -78°C, certain amounts of deionized water and HCl are slowly added thereto. Then, the flask is warmed to 70°C, at which temperature the flask is left for 20hrs so that the reaction could continue. At the completion of the reaction, the reaction mixture is transferred to a separatory funnel, followed

by addition of diethylether and tetrahydrofuran as much as the tetrahydrofuran used in the previous dilution of the monomer. Then, 3×washing is conducted, each round with water one tenth as much as the total solution in the separatory funnel. After washing, volatile materials are evaporated from the remaining solution to afford white powdery polymers. The powder was completely dissolved in a small amount of acetone to obtain a clear solution, and this solution is filtered through a 0.2μm syringe filter so as to remove impurities to provide a clear filtrate, to which is then slowly added deionized water. As a result, white powdery material is formed, which is then separated from the liquid phase(mixed solution of acetone and water) and dried for 10 hrs at a temperature of 0-20°C under a reduced pressure of about 0.1Torr to afford a siloxane-based resin. The results are shown in Table 5, below.

TABLE 5

Composition	Monomer (mmol)			HCl (mmol)	H ₂ O (mmol)	Final Resin (g)
	(A)	(B)	(C)			
(a)	12.32	9.17		0.12	250	6.87
(b)	13.87	11.62		0.22	548	8.84
(c)	10.55	4.67		0.16	485	8.54
(d)	10.55		4.67	0.145	514	7.89
(e)	10.55		4.67	0.145	857	8.23
(f)	10.55		4.67	0.131	514	8.98

COMPARATIVE EXAMPLE 2: Measurement of Dielectric Constant

[0038] Test pieces prepared as in the above comparative Example 1 are analyzed for thickness and refractive index using the same manner as the above Example 3, then analyzed for dielectric constant using the same manner as the above Example 4. The results are set forth in Table 6.

TABLE 6

Thin Film Composition			Dielectric Constant
Siloxane Resin	Resin (wt%)	Pore-forming Material (wt%)	
(a)	100	-	2.56
(a)	70	30	2.21
(b)	100	-	2.76
(b)	70	30	2.32
(c)	100	-	2.72
(c)	70	30	2.34
(e)	100	-	2.68
(e)	70	30	2.23
(f)	100	-	2.72
(f)	70	30	2.21
(g)	100	-	2.79
(g)	70	30	2.24
(a')	100	-	2.54
(a')	70	30	2.22
(b')	100	-	2.81
(b')	70	30	2.32
(c')	100	-	2.85
(c')	70	30	2.31
(d')	100	-	2.69
(d')	70	30	2.29
(e')	100	-	2.73
(e')	70	30	2.23
(f')	100	-	2.81
(f')	70	30	2.34

COMPARATIVE EXAMPLE 3: Measurement of Hardness and Modulus

[0039] Test pieces prepared as in the above comparative Example 1 are analyzed for thickness and refractive index using the same manner as the

above Example 3, then analyzed for hardness and elastic modulus using the same manner as the above Example 5. The results are set forth in Table 7.

TABLE 7

Thin Film Composition			Hardness (Gpa)	Modulus (Gpa)
Siloxane Resin	Resin (wt%)	Pore-forming Material (wt%)		
(a)	100	-	0.72	5.11
(a)	70	30	0.45	3.14
(b)	100	-	0.75	5.32
(b)	70	30	0.41	3.23
(c)	100	-	1.23	5.65
(c)	70	30	1.02	3.02
(e)	100	-	1.42	6.58
(e)	70	30	1.11	3.63
(f)	100	-	1.34	6.89
(f)	70	30	0.99	3.89
(g)	100	-	1.09	6.52
(g)	70	30	0.77	3.55
(a')	100	-	0.51	4.21
(a')	70	30	0.31	3.84
(b')	100	-	0.59	4.67
(b')	70	30	0.34	3.54
(c')	100	-	0.98	5.44
(c')	70	30	0.82	3.54
(e')	100	-	1.12	6.12
(e')	70	30	0.43	2.99
(f')	100	-	1.09	6.23
(f')	70	30	0.68	3.35
(g')	100	-	0.87	6.18
(g')	70	30	0.43	3.27

[0040] As apparent from Examples and Comparative Examples, the siloxane-based resin having germanium has relatively high hardness and modulus with a low dielectric constant.

[0041] Although the preferred embodiments of the present invention have been disclosed for illustrative purposes, those skilled in the art will appreciate that various modifications, additions and substitutions are possible, without

departing from the spirit and scope of the invention as recited in the accompanying claims.